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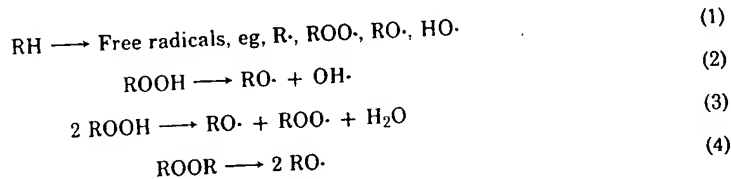
ANTIOXIDANTS

Antioxidants are used to retard the reaction of organic materials with atmospheric oxygen. Such reaction can cause degradation of the mechanical, aesthetic, and electrical properties of polymers; loss of flavor and development of rancidity in foods; and an increase in the viscosity, acidity, and formation of insolubles in lubricants. The need for antioxidants depends upon the chemical composition of the substrate and the conditions of exposure. Relatively high concentrations of antioxidants are used to stabilize polymers such as natural rubber and polyunsaturated oils. Saturated polymers have greater oxidative stability and require relatively low concentrations of stabilizers. Specialized antioxidants which have been commercialized meet the needs of the industry by extending the useful lives of the many substrates produced under anticipated conditions of exposure. The sales of antioxidants in the United States were approximately \$730 million in 1990 (1,2).

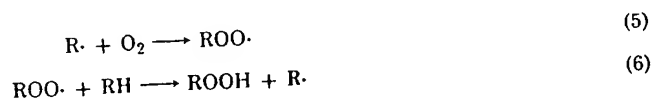
Mechanism of Uninhibited Autoxidation

The mechanism by which an organic material (RH) undergoes autoxidation involves a free-radical chain reaction (3-5):

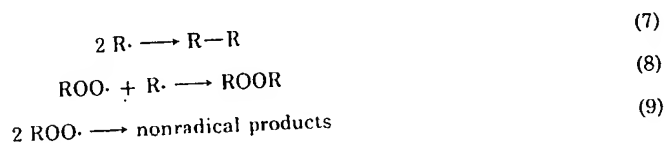
Initiation



Propagation



Termination



Initiation. Free-radical initiators are produced by several processes. The high temperatures and shearing stresses required for compounding, extrusion, and molding of polymeric materials can produce alkyl radicals by homolytic chain cleavage. Oxidatively sensitive substrates can react directly with oxygen, particularly at elevated temperatures, to yield radicals.

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PLASTIC BUILDING PRODUCTS. See BUILDING MATERIALS, PLASTIC.

PLASTICIZERS

A plasticizer is a substance the addition of which to another material makes that material softer and more flexible. This broad definition encompasses the use of water to plasticize clay for the production of pottery, and oils to plasticize pitch for caulking boats. A more precise definition of plasticizers is that they are materials which, when added to a polymer, cause an increase in the flexibility and workability, brought about by a decrease in the glass-transition temperature, T_g , of the polymer. The most widely plasticized polymer is poly(vinyl chloride) (PVC) due to its excellent plasticizer compatibility characteristics, and the development of plasticizers closely follows the development of this commodity polymer. However, plasticizers have also been used and remain in use with other polymer types.

The amount of plasticizer added to the polymer in question varies, depending on the magnitude of the effect required. For example, a small addition of plasticizer may be made simply to improve the workability of the polymer melt. This contrasts with larger additions made with the specific intention of completely transforming the properties of the product. For example, PVC without a plasticizer, ie, unplasticized PVC (PVC-U), is used in applications such as pipes and window profiles; with plasticizer added, articles such as PVC food film, PVC cable insulation, and sheathing and PVC floorings are formed.

There are presently ~300 plasticizers in manufacture. Of these ~100 are of commercial importance. A list of some common commodity and speciality plasticizers are given in Table 1.

Types of Plasticizers

Two principle methods exist for softening a polymer to bring about the dramatic effects of plasticization. A rigid polymer may be internally plasticized by chemically modifying the polymer or monomer so that the flexibility of the

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PHOSPHORUS FLAME RETARDANTS

One of the principal classes of flame retardants used in plastics and textiles is that of phosphorus, phosphorus-nitrogen, and phosphorus-halogen compounds (see also FLAME RETARDANTS FOR TEXTILES). Detailed reviews of phosphorus flame retardants have been published (1-6) (see also PHOSPHORUS COMPOUNDS).

Mechanisms of Action

Condensed-Phase Mechanisms. The mode of action of phosphorus-based flame retardants in cellulosic systems is probably best understood. Cellulose (qv) decomposes by a noncatalyzed route to tarry depolymerization products, notably levoglucosan, which then decomposes to volatile combustible fragments such as alcohols, aldehydes (qv), ketones (qv), and hydrocarbons (qv) (7-9). However,

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when catalyzed by acids, the decomposition of cellulose proceeds primarily as an endothermic dehydration of the carbohydrate to water vapor and char. Phosphoric acid is particularly efficacious in this catalytic role because of its low volatility (see PHOSPHORIC ACID AND THE PHOSPHATES). Also, when strongly heated, phosphoric acid yields polyphosphoric acid which is even more effective in catalyzing the cellulose dehydration reaction. The flame-retardant action is believed to proceed by way of initial phosphorylation of the cellulose. Certain nitrogen compounds such as melamines, guanidines, and ureas appear to catalyze the cellulose phosphorylation step and are found to enhance or synergize the flame-retardant action of phosphorus on cellulose (10-13). The nonvolatile phosphorus acids are also able to coat the char, rendering the char less permeable and protecting it from further oxidation. The retention of phosphorus in the char may be aided by the nitrogen synergists.

In poly(ethylene terephthalate) (14-16) and poly(methyl methacrylate) (17-19), the mechanism of action of phosphorus flame retardants is at least partly attributable to a decrease in the amount of combustible volatiles and a corresponding increase in nonvolatile residue (char). In poly(methyl methacrylate), the phosphorus flame retardant appears to cause an initial cross-linking through anhydride linkages (19).

The amount and physical character of the char from rigid urethane foams is found to be affected by the retardant (20-23) (see FOAMS; URETHANE POLYMERS). The presence of a phosphorus-containing flame retardant causes a rigid urethane foam to form a more coherent char, possibly serving as a physical barrier to the combustion process. There is evidence that a substantial fraction of the phosphorus may be retained in the char. Chars from phenolic resins (qv) were shown to be much better barriers to pyrolysis vapors and air when ammonium phosphate was present in the original resin (24). This barrier action may at least partly explain the inhibition of glowing combustion of char by phosphorus compounds.

In polymers such as polystyrene that do not readily undergo charring, phosphorus-based flame retardants tend to be less effective, and such polymers are often flame retarded by antimony-halogen combinations (see STYRENE POLYMERS). However, even in such noncharring polymers, phosphorus additives exhibit some activity that suggests at least one other mode of action. Phosphorus compounds may produce a barrier layer of polyphosphoric acid on the burning polymer (4,5). Phosphorus-based flame retardants are more effective in styrenic polymers blended with a char-forming polymer such as a polyphenylene oxide or polycarbonate.

Phosphorus-containing additives can act in some cases by catalyzing thermal breakdown of the polymer melt, reducing viscosity and favoring the flow or drip of molten polymer from the combustion zone (25). On the other hand, red phosphorus [7723-14-0] has been shown to retard the nonoxidative pyrolysis of polyethylene (a radical scission). For that reason, the scavenging of radicals in the condensed phase has been proposed as one of several modes of action of red phosphorus (26).

Several commercial polyester fabrics are flame retarded using low levels of phosphorus additives that cause them to melt and drip more readily than fabrics without the flame retardant. This mechanism can be completely defeated by the presence of nonthermoplastic component such as infusible fibers, pigments, or by